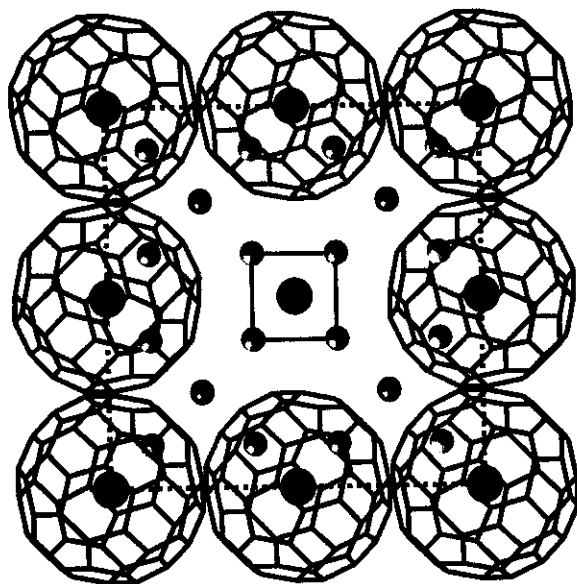
 <b>ESRF</b>	<b>Experiment title:</b> Structural studies of fullerene derivatives	<b>Experiment number:</b> CH-507
<b>Beamlines:</b> BM1/BM16	<b>Date of experiment:</b> from: 12/11/98 to: 15/11/98 and 8/12/98 to: 14/12/98	<b>Date of report:</b> 5/3/99
<b>Shifts:</b> 9/9	<b>Local contact(s):</b> K Knudsen / A N Fitch	<i>Received at ESRF:</i> <b>15 MAR. 1999</b>
<b>Names and affiliations of applicants (* indicates experimentalists):</b> S Margadonna,* D Arcon,* N Tagmatarchis,* and K Prassides*  School of Chemistry, Physics and Environmental Science, University of Sussex, Brighton BN1 9QJ, UK  M Kosaka and K. Tanigaki  Fundamental Research Laboratories, NEC Corporation, 34 Miyukigaoka, Tsukuba 305-8501, Japan		

### Report:

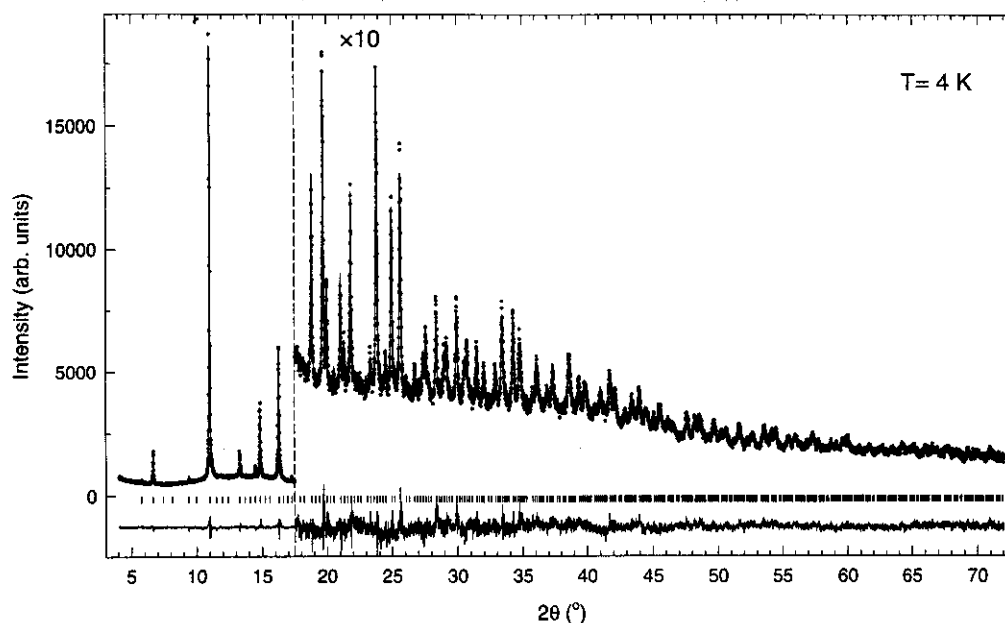
Alkali fullerides with stoichiometry  $A_2A'C_{60}$  ( $A, A'$  = alkali metals) are superconducting with  $T_C$  at ambient pressure ranging from 3.5 K for  $Na_2RbC_{60}$  to 33 K for  $RbCs_2C_{60}$ . The only exception to this behavior has been provided by  $Li_2CsC_{60}$  and  $Li_2RbC_{60}$  which were found not to show superconductivity down to 50 mK. The absence of superconductivity in the Li fulleride family has been associated with the presence of strong bonding  $Li^+$ -C interactions. As a result, the formal charge of the  $C_{60}^{n-}$  ions in  $Li_2A'C_{60}$  is less than 3, implying a less than half full  $t_{1u}$  band. In an attempt to overcome the intercalate-carbon interactions and achieve half filling ( $n=3$ ) of the  $t_{1u}$  band, we synthesized the family of lithium fulleride salts,  $Li_xCsC_{60}$  with  $x$  ranging from 1.5 to 6. By adjusting the Li content,  $x$ , we can control the electron transfer from the alkali metals to  $C_{60}$  and tune the filling level of the conduction band continuously. Half filling is achieved for the composition  $Li_3CsC_{60}$  which is a bulk superconductor with  $T_c=10.5$  K.

In these experiments, we addressed the problem of the structural properties of the  $Li_3CsC_{60}$  superconductor. At low temperatures, its crystal structure is primitive cubic (space group  $Pa\bar{3}$ ) isostructural with the metastable phases of the superconducting  $Na_2A'C_{60}$  salts with orientationally ordered  $C_{60}^{3-}$  ions present in the unit cell (Fig. 1). The tetrahedral and octahedral interstices of the structure are occupied by the Li and Cs cations, respectively,

while the excess Li (one per  $C_{60}$  unit) is disordered at the corners of a cube with an edge length of  $\sim 3.4$  Å, centered at the octahedral sites. On heating to room temperature, a phase transition occurs to a *fcc* structure (space group  $Fm\bar{3}m$ ) which contains orientationally disordered  $C_{60}^{3-}$  ions. The results provide clear evidence of the importance of the  $Li^+$ -C interactions in sensitively controlling the structural, conducting and electronic properties of the family of lithium intercalated fullerenes.



**Fig. 1** Basal plane projection of the primitive cubic structure of  $Li_3CsC_{60}$ , showing the Li defect geometry, centered at the  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  position in the unit cell.



**Fig. 2** Final observed (○) and calculated (solid line) synchrotron X-ray diffraction profiles for  $Li_3CsC_{60}$  at 4 K ( $\lambda = 0.81073$  Å, space group  $Pa\bar{3}$ ). The lower solid line shows the difference profile and the tick marks show the reflection positions. The profile has been expanded for clarity by a factor of 10 at Bragg angles larger than  $17.5^\circ$ .